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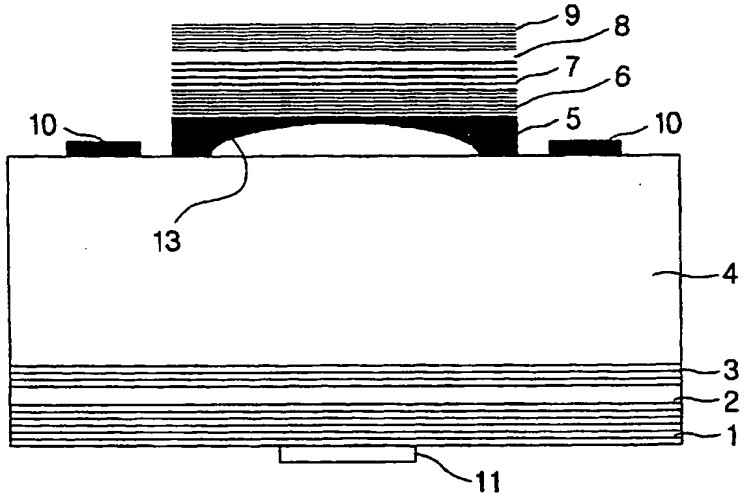
(54) Title: METHOD OF MANUFACTURING AN InGaNAs COMPOUND SEMICONDUCTOR THIN FILM AND THE THIN FILM MANUFACTURED BY THE SAME



(57) Abstract: Disclosed is a method of manufacturing an InGaNAs compound semiconductor thin film and the thin film manufactured by the same. The method of manufacturing the InGaNAs compound semiconductor thin film used as a structural element of a compound semiconductor device, wherein a plurality of precursors are deposited using a deposition apparatus comprises the steps of preparing at least one metal organic compound containing molecular Ga-N as the precursors, and providing nitrogen atoms from such metal organic compound to a reactor in the deposition apparatus during a deposition process for growth of the InGaNAs film so as to distribute the nitrogen atoms in a predetermined concentration within the InGaNAs thin film. Hence, detachment of nitrogen atoms can be prevented by means of strong bonding strength of Ga(Al,In)-N molecules, whereby the content of nitrogen atoms within the InGaNAs can be effectively regulated under control of inflow of the precursors used for providing the nitrogen atoms.

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METHOD OF MANUFACTURING AN InGaNAs COMPOUND SEMICONDUCTOR THIN FILM AND THE THIN FILM MANUFACTURED BY THE SAME

TECHNICAL FIELD

The present invention relates, in general, to a method of manufacturing an InGaNAs compound semiconductor thin film and the thin film manufactured by the same, and more specifically, to a method of manufacturing an InGaNAs compound semiconductor thin film of a compound semiconductor capable of introducing ing effectively the nitrogen component in a desired concentration to the InGaNAs thin film from a metal organic compound containing a Ga(Al,In)-N molecule and the thin film manufactured by the same.

BACKGROUND ART

In recent years, nitride-based semiconductors, which are the Group III-V compound semiconductors containing a nitrogen component, have received a great deal of attention as new materials for use in an optical communication and electrical and electronic fields. Such nitride-based semiconductors are expected to cope with technical limitations experienced in the optical and electronics industries due to properties of conventional silicon and compound semiconductors, and also to improve conventional industries, with development of new industries realizing high added value.

Particularly, an InGaNAs/GaAs material system of four novel elements is suitable for use as a direct band gap material to emit light within wavelength of about 1.3-1.55 μm on a substrate such as GaAs. So, research on application of such material to a long-wavelength laser diode (LD) or a long-wavelength surface emitting semiconductor laser (VCSEL) for an optical light source of an optical communication has been vigorously carried out.

Consequently, according to an embodiment of an InGaNAs thin film formation method used at present, the InGaNAs thin film can be fabricated by use of

precursors containing Ga, In, Al, N and As, for instance, four organic reactants of TMIn (trimethyl indium), TMGa (trimethyl gallium), NH_3 and AsH_3 through MOCVD (metalorganic chemical vapor deposition) process.

As such, the used MOCVD process is a technique for preparing a thin film by means of a thermal chemical vapor deposition using metal organic compounds. This technique, similar to MBE (molecular beam epitaxy) process, has been under study to achieve growth of very thin crystalline film, manufacture of multilayered structures, control of variously mixed compositions, and mass production of compound semiconductors.

In addition, the MOCVD process has the following advantages: first, a semiconductor device with one heating place comprises a simplified structure and thus can be easily designed as a mass production device; second, a growth rate of the film can be determined by gas inflow, so easily regulating such rate; third, growth of crystals can be performed under control of on-off state of a valve and inflow of each gas; fourth, epitaxial growth can be carried out on an Al_2O_3 insulation layer, and selective epitaxial growth can be conducted; fifth, a substrate or a device is not etched because of no introduction of halogenides, such as HCl, during growth reaction.

However, the MOCVD process has the disadvantages of generating large quantities of residual impurities, uncontrollable thickness of crystals, flammable and toxic reaction gases, and expensive raw materials.

Meanwhile, in order to use the InGaNAs materials as a long-wavelength laser diode (LD) for an optical light source of an optical communication, the concentration of nitrogen atoms (N) inside the InGaNAs film should be suitably controlled so that the thin film can function with respect to a specific wavelength.

But in the case of fabricating the InGaNAs compound semiconductor thin film by use of such conventional method and device, when nitrogen atoms are added to the grown InGaNAs film from NH_3, the nitrogen atoms are easily detached from the grown surface due to low solubility of nitrogen to the InGaNAs film and high equilibrium vapor pressure at 600 °C or higher, whereby it is difficult to provide sufficient nitrogen atoms to the film. Thus, excellent optical properties cannot be conferred on long-wavelength optical devices, such as long-wavelength laser diode

(LD) and long-wavelength VCSEL.

Additionally, since metal organic reactants are present on the grown surface during film growth, the nitrogen component is not located to an original position and the concentration of nitrogen atoms within the film is not increased.

Further, nitrogen atoms independently move on the thin film grown surface and are thus misplaced to the Group III position, or form undesirable nitrides, thereby lowering the properties of the device.

Therefore, it is an object of the present invention to alleviate the problems in the prior art and to provide a method of manufacturing an InGaNAs compound semiconductor thin film, capable of preventing detachment of nitrogen atoms at growth temperatures of 600 °C or higher and easily controlling the content of nitrogen atoms by adjustment of the amount of organic reactants containing Ga-N used as a precursor; and the film manufactured by the same.

DISCLOSURE OF THE INVENTION

In order to accomplish the above object, a method of manufacturing the InGaNAs compound semiconductor thin film of the present invention is characterized in that the method of manufacturing the InGaNAs compound semiconductor thin film from a plurality of precursors using the deposition apparatus comprises the steps of preparing at least one metal organic compound containing Ga-N of molecular form as the precursors, and providing nitrogen atoms from such metal organic compound containing Ga-N of molecular form to a reactor of the deposition apparatus during a deposition process for growth of the InGaNAs thin film so as to distribute the nitrogen atoms in a predetermined concentration within the InGaNAs thin film.

As the plurality of precursors used in the present invention, a member selected from the group consisting of TMIn, TEIn, DMIn and DEIn, a member selected from the group consisting of TMGa, TEGa, DMGa and DEGa, and AsH_3 are used, along with the Ga-N molecule-containing metal organic compound which is preferably selected from group of consisting of H_2GaN_3, Cl_2GaN_3, $Ga_2(NH_3)_{3/2}$ and $Ga_2(N(CH_3)_2)_6$.

In addition, it is preferred that MOCVD (metalorganic chemical vapor deposition) or MBE (molecular beam epitaxy) apparatus is used as the deposition apparatus.

In addition, an InGaNAs compound semiconductor thin film formed by the above-mentioned methods is disclosed in the present invention.

Further, a compound semiconductor device provided with the above InGaNAs compound semiconductor thin film is disclosed in the present invention.

The inventive method is characterized in that the nitrogen atoms are effectively introduced to the film by use of gallium (Ga) and nitrogen (N) in molecular form charged into the reactor. That is to say, the metal organic compound comprising Ga-N in the molecular form is added to the reactor, together with other three organic reactants of TMIn, TMGa and AsH_3, and then subjected to general MOCVD process, yielding the InGaNAs thin film. As such, the Ga-N molecules remain in bonded state because of strong bonding strength between gallium and nitrogen atoms, even though other radicals are decomposed at general reactor temperature (about 700 °C). When such Ga-N molecules reach the growth surface, the gallium component is automatically placed to the Group III position and the nitrogen component is also automatically placed to the Group V position. In other words, since detachment of the nitrogen component is prevented due to a strong bonding with gallium, quantities of nitrogen atoms can be introduced to the desired position. Further, such Ga-N molecular form is low in mobility to the growth surface and thus formation of nitrides, by-products of the reactions can be prevented.

Therefore, the content of nitrogen atoms can be simply, easily and precisely adjusted under the control of inflow of the metal organic compound, in the InGaNAs thin film functioning as an important element emitting wavelengths of 1,200-1,600 nm, preferably, 1,310-1,550 nm, from a long-wavelength laser diode for an optical light source of an optical communication system. The optical device having more excellent optical properties can be provided at a low price, compared to conventional optical devices.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows schematically a structure of gaseous H_2GaN_3 trimer (N_2 portions in N_3 groups are omitted).

FIG. 2 shows schematically a structure of gaseous Cl_2GaN_3 trimer.

FIG. 3 is a cross sectional view showing an illustration of a surface emitting semiconductor device containing an InGaNAs compound semiconductor thin film of the present invention.

BEST MODES FOR CARRYING OUT THE INVENTION

In the examples as stated below, deposition of the InGaNAs thin film is illustrated using some organic reactants containing Ga-N molecules as precursors.

EXAMPLE 1

In the present example H_2GaN_3 was used as a precursor providing Ga-N molecules. Such H_2GaN_3 is sensitive to air at room temperature and is a volatile liquid, which is capable of producing vapor at about 40 °C (0.200 Torr) and exists as a trimer form in gas state. The structure of gaseous H_2GaN_3 trimer is shown in FIG. 1, in which N_2 portions of N_3 groups are omitted for clearer understanding the drawing.

Reaction 1

$$H_2GaN_3 \rightarrow GaN + H_2 + N_2$$

The above reaction 1 shows the decomposition process of H_2GaN_3 to a Ga-N molecule, a hydrogen molecule and a nitrogen molecule. Such reaction was easily performed at relatively low temperature of about 150 °C, and did not produce impurities including carbon, oxygen molecules, etc., upon formation of the Ga-N molecule. Thus, since other materials, exclusive of gallium and nitrogen atoms, were not introduced to the reaction, the content of the nitrogen atom could be precisely controlled.

In the present example, three organic materials including TMGa, TMIn

and AsH_3, and a metal organic compound, H_2GaN_3, were charged into a reactor and then subjected to MOCVD process, to deposit an InGaNAs thin film as represented in the following reaction 2.

Reaction 2

$TMGa + TMIn + H_2GaN_3 + AsH_3 \rightarrow InGaNAs + H_2 + N_2$ + other organic materials (radical)

EXAMPLE 2

In the present example, Cl_2GaN_3 was used as the precursor for provision of the Ga-N molecule. Such Cl_2GaN_3 reacts in a trimer form in the temperature range of 500 to 700 °C. FIG. 2 shows a schematic structure of the expectant Cl_2GaN_3 trimer.

Reaction 3

$3Cl_2GaN_3 \rightarrow GaN + 2GaCl_3 + 4N_2$

The above reaction shows the decomposition process of Cl_2GaN_3 to a Ga-N molecule, a gallium chloride and a nitrogen molecule. In such reaction, impurities including carbon, oxygen molecules, etc., were not produced upon formation of the Ga-N molecule, similarly to the above example 1. Accordingly, the content of the nitrogen atom could be effectively and precisely controlled through control of inflow of Cl_2GaN_3 due to no addition of impurities other than gallium and nitrogen atoms.

In the present example, similar to the example 1, into the reactor, three organic materials of TMGa, TMIn and AsH_3, and a metal organic compound, Cl_2GaN_3, were charged and then subjected to MOCVD process, to deposit the InGaNAs thin film as represented in the following reaction 4.

Reaction 4

$TMGa + TMIn + Cl_2GaN_3 + AsH_3 \rightarrow InGaNAs + Cl_2 + N_2$ + other organic materials (radical)

In the present InGaNAs film formation method, the metal organic

compound including Ga-N of molecular form was utilized, instead of conventionally used NH_3, whereby problems related to conventional deposition process were solved and the compound semiconductor device having excellent optical properties could be fabricated, with the use of a conventional device and method.

EXAMPLE 3

In the present example a compound semiconductor device having the thin film prepared by the inventive method is described with reference to the appended drawing. Such compound semiconductor device is illustrated as an embodiment applied with the InGaNAs compound semiconductor thin film. Thus the present invention is not defined to the present example.

FIG. 3, which is disclosed in Korean Patent Application No. 2001-64829, filded by the present inventors, shows a cross sectional view of vertically integrated surface emitting semiconductor laser device having high output (hereinafter, referred to as "compound semiconductor device").

Referring to FIG. 3, there is shown the compound semiconductor device comprising a first light-emitting structure, a second light-emitting structure, a substrate, an optical lens and at least one pair of electrodes. More specifically, the first light-emitting structure consists of a lower DBR (distributed Bragg reflector) 1 with regard to a first wavelength, an active layer 2 (cavity), a first upper DBR 3 with regard to the first wavelength and a second upper DBR 6 with regard to the first wavelength. The lower DBR 1 and the first upper DBR 3 with regard to the first wavelength are doped to p-type and n-type, respectively, thus having electrical conductivity. An n-type GaAs substrate 4 is located between the first upper DBR 3 and the second upper DBR 6 with regard to the first wavelength. In addition, an optical lens 13 formed by wet-oxidizing an AlGaAs layer 5 is further disposed between the first upper DBR 3 and the second upper DBR 6 with regard to the first wavelength. The second light-emitting structure is composed of a lower DBR 7 with regard to a second wavelength, an active layer 8 (cavity) and an upper DBR 9 with regard to the second wavelength. The second light-

emitting structure is placed on the second upper DBR 6 with regard to the first wavelength. On a circumferential periphery of the n-type GaAs substrate 4 facing the second light-emitting structure, n-type electrodes 10 are positioned, and on the back face of the substrate 4 is positioned a p-type electrode 11, adjacent to the lower DBR 1 of the first wavelength.

The InGaNAs compound semiconductor thin film manufactured by the method of the present invention is formed as the active layer 8 in the compound semiconductor device.

As described in the above examples 1 and 2, the InGaNAs thin film of the compound semiconductor device is fabricated using the metal organic compound including Ga-N of molecular form as the precursor, whereby optical devices, such as LD, VCSEL, etc., having excellent optical properties over the wavelength range of from 1,200 to 1,600 nm can be provided.

In addition, as the precursors, one member selected from among TMIn (trimethyl indium azide), TEIn (triethyl indium azide), DMIn (dimethyl indium azide) and DEIn (diethyl indium azide) and the other member selected from among TMGa, TEGa, DMGa and DEGa, can be used, along with AsH_3 and the metal organic compound containing Ga-N of molecular form.

Further, as the precursor of supplying Ga-N molecule, suitable other metal organic compounds, such as $Ga_2(NH_3)_{3/2}$, $Ga_2(N(CH_3)_2)_6$, etc., may be used, other than the metal organic compound of H_2GaN_3 and Cl_2GaN_3 used in the above examples.

The present invention is not defined to the examples using the metal organic compound containing Ga-N of molecular form, and Al-N or In-N metal organic compound which has similar physical and chemical properties to Ga-N molecule may be used to form the InGaNAs film.

Though the InGaNAs thin film was deposited by means of MOCVD method in the above examples, the other appropriate deposition methods, such as MBE (molecular beam epitaxy), can be used to deposit the InGaNAs thin film, within the technical scope of the present invention.

INDUSTRIAL APPLICABILITY

As described above, the detachment of nitrogen atoms can be prevented due to strong bonding strength of a Ga-N molecule at high temperatures of up to 700 °C.

Thereby, there is the advantage of efficient control of the content of nitrogen atoms within the InGaNAs thin film due to control of inflow of precursors used for providing the nitrogen atoms. This means that the optical devices, such as VCSEL, of the wavelength ranging from 1,200 to 1,600 nm, can be easily fabricated.

Additionally, the nitrogen atoms can be provided in the Ga-N molecular form and thus defects caused by nitrogen atom misplacement to the Group III position or formation of undesired nitrides can be prevented. Therefore, the optical devices having very excellent optical properties of the InGaNAs thin film can be provided.

CLAIMS

1. A method of manufacturing an InGaNAs compound semiconductor thin film from several precursors using a deposition apparatus, comprising the steps of:

preparing at least one metal organic compound containing Ga-N of molecular form as the precursors; and

providing nitrogen atoms from said metal organic compound containing Ga-N of molecular form to a reactor of the deposition apparatus during a deposition process for growth of the InGaNAs thin film so as to distribute the nitrogen atoms in a predetermined concentration within the InGaNAs thin film.

2. The method as defined in claim 1, wherein said several precursors further comprise a member selected from the group consisting of TMIn, TEIn, DMIn and DEIn, a member selected from the group consisting of TMGa, TEGa, DMGa and DEGa, and AsH_3, and said metal organic compound containing Ga-N of molecular form is a member selected from the group consisting of H_2GaN_3, Cl_2GaN_3, $Ga_2(NH_3)_{3/2}$ and $Ga_2(N(CH_3)_2)_6$.

3. The method as defined in claim 1, wherein said deposition apparatus is a metalorganic chemical vapor deposition apparatus or a molecular beam epitaxy apparatus.

4. An InGaNAs compound semiconductor thin film manufactured by method of any one of claims 1 to 3.

5. A compound semiconductor device comprising the InGaNAs compound semiconductor thin film of claim 4.

FIG. 1

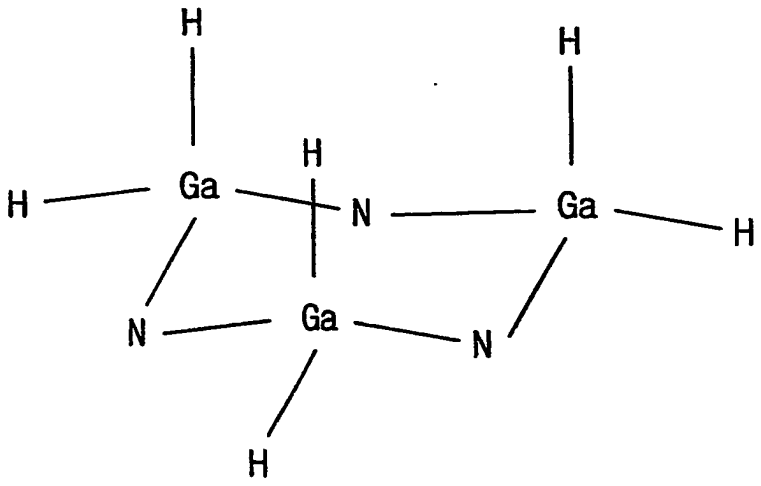


FIG. 2

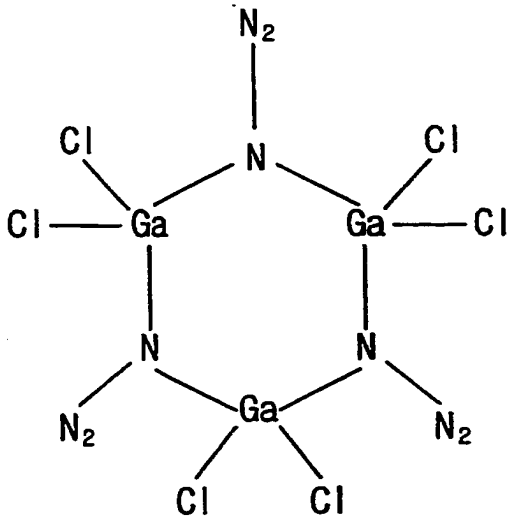
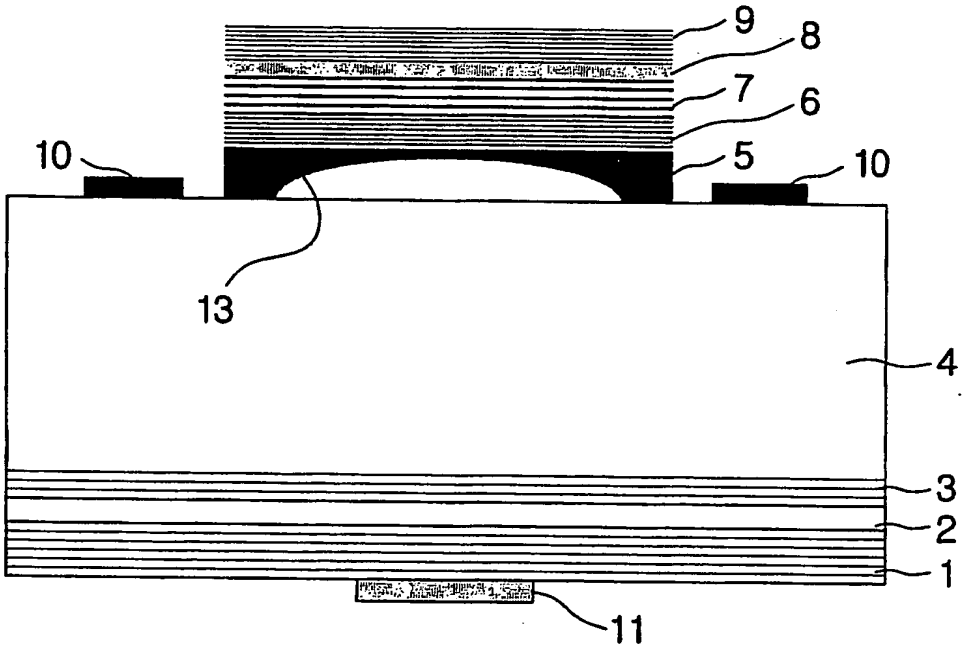


FIG. 3



INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC7 H01L 21/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H)1L 33/00, H01L 5/343, H01S 3/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search terms used)

USPAT, PAJ, FPD

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, A 10233557 (RICOH CO LTD) 2 September 1997 see abstract, paragraph 12 - 15	1
Y	JP, A 2001094151 (SHARP CORP) 6 April 2001 see abstract, paragraph 88 - 91	1
A	JP, A 10075017 (RICOH CO LTD) 17 March 1998 see the whole document	1

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevence
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